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(54) COATED HARD ALLOY

(57)Abstract

PURPOSE: To reduce the residual compressive stress of an alloy, to increase the adhesiveness of a film, furthermore to improve the peeling resistance of a coated tool and simultaneously to thicken the film by adding elements having hardness lower than that of TiN and TiAlN and allowing the same to enter into solid solution.

CONSTITUTION: In the case the compsn. of a film of a film hard alloy of coating hard metal in which a part of Ti in the hard film with 0.5 to 10 μ m film thickness consisting essentially of Ti and Al and/or the nitrides and carbides of the solid solution thereof is substituted by Fe-based metal and/or Cr is expressed by (Ti_aAl_bFe-based cCr_d), (a), (b), (c), (d) and (x) are respectively regulated to the ranges of a+b+c+d=1, a: 0.3 to 0.7, b: 0.3 to 0.7, c: 0.01 to 0.2, d: 0 to 0.1 and x: 0 to 1. Thus, the defect of the high residual stress of a PVD film is improved, by which the service life of a coated cutting tool can be prolonged.

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CLAIMS

[Claim(s)]

[Claim 1] This coat composition of the covering hard metal which replaced the one section of Ti of the hard anodic oxidation coatings which consists of the 0.5-10-micrometer thickness which consisted of Ti, aluminum and/or a nitride of the solid solution, and a charcoal nitride as a principal component by Fe group metal and/or Cr is set to a mole ratio. (Ti a Al b Fe group c Cr d) When expressed C_xN_{1-x} , a, b, c, d, and x are $a+b+c+d=10.3$, respectively. $0 \leq a \leq 0.70.3$ $0 \leq b \leq 0.70.01$ $0 \leq c \leq 0.20$ $0 \leq d \leq 0.10$ Covering hard metal characterized by being the coat of the domain which consists of $0 \leq x \leq 1$.

[Claim 2] The covering hard metal characterized by making into the multilayer of five or more layers the layer of a nitride [having replaced a part of Ti by Fe and/or Cr (TiFeCr)], and a charcoal nitride, and the layer which consists of the nitride of aluminum in a covering hard metal according to claim 1.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] The invention in this application relates to the covering abrasion-resistant member used as the covering cutting-tool member and antifriction tool which are used as a cutting tool which is excellent in abrasion resistance and deficit-proof nature.

[0002]

[Description of the Prior Art] although the hard anodic oxidation coatings by the conventional PVD had TiN in use -- recently -- TiCN layer -- or (TiAl) the coat of the new modality of N is developed and has attracted attention TiCN has 3000--about Vickers hardness number, and it also has the effect which is markedly alike compared with Vickers hardness number 2200 of TiN, and raises abrasion resistance remarkably firmly On the other hand (TiAl), although N changes with proportion of Ti and aluminum, it has the Vickers hardness number of outlines 2300--2800, and since which raises abrasion resistance compared with TiN] oxidation resistance is remarkably excellent on the other hand, the property excellent in the bottom of the cutting conditions from which the edge of a blade becomes an elevated temperature etc. is demonstrated.

[0003] Moreover, as an improvement of the coat of N (TiAl) layer, JP,5-67705,B which limited the proportion of Ti/aluminum, U.S. JP,4871434,B which is called N (TiAlZr) and N (TiAlV) and which was further used as the coat of plural systems are proposed, and the improvement is measured further. However, although these new coats have the above-mentioned advantage, its compressive stress which remains to a coat is as high as 1.5 or more times of TiN coat, and it has the following various troubles.

[0004]

[Problem(s) to be Solved by the Invention] The adhesion force of a coat becomes so weak that the residual compression stress of a coat becomes high, and these new coats are inferior in the adhesion compared with TiN. Moreover, as for this residual stress being high, it is also the present condition that thick-film-ization is not realized for a technical failure to thick-film-izing of a coat in the adhesion of a coat since it not only worsens, but residual stress increases as a thickness becomes thick.

[0005] The easiest method of reducing a residual compression stress can consider changing the covering parameter in a covering process. When 3 micrometers of TiNs were formed to up to a steel substrate by the arc ion electric discharge method and this invention person investigated the residual compression stress of the ** system partial pressure which is a covering parameter, and bias voltage, he showed the residual compression stress of -5GPa in -2GPa and identity-100V in bias voltage-50V. moreover, a ** system partial pressure -- the bottom of 10-1Pa -- setting -1GPa -- said -- the residual compression stress of -2GPa was shown in 100Pa Thus, although the residual compression stress could be easily changed by changing a coat parameter, in the arc ion electric discharge method and ***** lied way etc., it was impossible to have reduced a residual compression stress by changing a parameter as a matter of fact for the ground of the thing for which it has the domain of each optimum parameter, and the layer properties of the coat formed by change of a parameter completely differing.

[0006]

[Objects of the Invention] It offers the technique which also enables thick-film-ization at the same time it improves the peeling resistance of a covering tool, if an above-mentioned residual compression stress improves a high fault, this invention raises the adhesion of a coat by reducing a residual compression stress and it is forced it.

[0007]

[Means for Solving the Problem] Then, this invention acquired the following knowledge, as a result of performing the study which adds various elements to this on the basis of N (TiAl). Table 1 shows each residual compression stress at the time of setting the residual compression stress of 3-micrometer TiN to 1 for the residual compression stress at the time of adding various elements, when forming 3 micrometer(TiAl) N coat by the arc ion-plating method under the condition of a ten to 1 Pa bias voltage 120V ** system pressure.

[0008]

[Table 1]

番号	組成	残留圧縮応力度
従来例	1 TiN	1.0
	2 Ti _{0.5} Al _{0.5} N	3.1
	3 Ti _{0.4} Al _{0.6} N	3.2
	4 Ti _{0.45} Al _{0.45} V _{0.1} N	3.0
	5 Ti _{0.45} Al _{0.45} Zr _{0.1} N	3.0
	6 Ti _{0.45} Al _{0.45} Hf _{0.1} N	3.0
	7 Ti _{0.45} Al _{0.45} Ta _{0.1} N	3.2
	8 Ti _{0.45} Al _{0.45} Nb _{0.1} N	3.7
本発明例	9 Ti _{0.45} Al _{0.45} Co _{0.1} N	1.8
	10 Ti _{0.45} Al _{0.45} Ni _{0.1} N	1.4
	11 Ti _{0.45} Al _{0.45} Fe _{0.1} N	1.4
	12 Ti _{0.45} Al _{0.45} Co _{0.05} W _{0.05} N	2.5
	13 Ti _{0.45} Al _{0.45} Ni _{0.05} Cr _{0.05} N	2.0
	14 Ti _{0.45} Al _{0.45} Ni _{0.05} Mo _{0.05} N	2.3

[0009] That there is an inclination that the residual stress in a layer decreases understands an elasticity metal variance or by making it solid-solution-ize in N (TiAl) coat from Table 1. The invention in this application as a principal component Therefore, Ti, aluminum, and/or the nitride of the solid solution, This coat composition of the covering hard metal which replaced the one section of Ti of the hard anodic oxidation coatings which consists of the 0.5–10–micrometer thickness which consisted of a charcoal nitride by Fe group metal and/or Cr is set to a mole ratio. (TiAlb Fe group c Crd) When expressed CxN1–x, a, b, c, d, and x are a+b+c+d=10.3, respectively. $\leq a \leq 0.70.3$ $\leq b \leq 0.70.01$ $\leq c \leq 0.20$ $\leq d \leq 0.10$ It is the coat which consists of $\leq x \leq 1$, and those coats are further made into the multilayer of five or more layers, and thick-film-ization is attained.

[0010]

[Function] (TiAl) By adding Fe group and Cr in the coat of a compound, the residual stress in a layer is decreased and it becomes the layer which seldom exfoliates also to membranous shock resistance and the impact with especially mechanical intermittence cutting etc. Furthermore, if the alloyed target is used in the case of Fe group, a part of aluminum can be formed as compounds (NiAl), such as (CoAl), and the abrasion resistance of a coat, oxidation resistance, etc. can be doubled and improved. Cr group's case also has the same effect and oxidation resistance, thermal resistance, etc. are improved. Hereafter, it attaches and explains to the ground for having carried out numerical limitation.

[0011] (TiAl) Fe group who adds as the solid solution/a mixture in a compound layer did not have effect sufficient by less than 0.01 to reduce residual stress, and since the amount of Fe group in a coat would increase too much and abrasion resistance, welding-proof nature, etc. would deteriorate if 0.2 is exceeded, he was taken as the domain of $0.01 \leq c \leq 0.2$. Moreover, since the amount of Cr added as the solid solution/a mixture in a compound (TiAl) layer of Cr in a coat would increase too much and sufficient effect for a reduction of residual stress would be lost if it is made to alloy with Fe group, the oxidation resistance etc. is raised and it adds exceeding 0.1, although Fe group's content is correlated, it was taken as the domain of $0 \leq d \leq 0.1$. In addition, whether it solid-solution-izes as target material or the above-mentioned element adjusts a component for each element as an individual target at the time of vacuum evaporation, even if it combines a solid-solution target and an individual target further, it does the same effect so.

[0012] Having made proportion of CN in a coat into the domain of $0 \leq x \leq 1$, i.e., carbide, a nitride, and a charcoal nitride Since stress is eased by Fe group who added as the solid solution/a mixture in the layer, and the effect of Cr, (TiAl) Since it had sufficient performance by fully also being able to use the carbide with high hardness, and adjusting Fe group and the amount of Cr also in a little low nitride of hardness, and a charcoal nitride, it considered as the domain of $0 \leq x \leq 1$. Hereafter, an example explains the invention in this application in detail.

[0013]

[Example] 2.5 micrometers commercial WC powder, 1.5–micrometer TiC powder, this TiN powder, and 1.2–micrometer TaC powder were mixed with the ball mill for 96 hours so that it might become composition of 84WC–3TiC–1TiN–3TaC–9Co, TA insertion of SNMA432 was pressed after the xeransis granulation, and the predetermined configuration was processed after sintering. On this cemented-carbide base, by PVD, various alloy targets and the target element independent [each] were prepared, and a coat which is shown in Table 2 was formed. In addition, it was attached to the layer indicated in the conventional example for the comparison. Subsequently, with the scratch circuit tester, these coats are raised gradually, the load is scratched from 0, and the load against which a layer exfoliates was searched for. Those results are shown in Table 2.

[0014]

[Table 2]

	磨削	磨粒	スクラッチ 硬度 (N)	切削寿命 (min)
本発明合金	9	4	20	65 (正常摩耗)
	10	4	25	65 (")
	11	4	25	70 (")
	12	4	28	85 (")
	13	4	29	75 (")
	14	4	26	62 (")
従来例	1	4	20	25 (正常摩耗)
	2	4	26	35 (正常摩耗)
	3	4	22	32 (正常摩耗)
	4	4	18	8 (腐蝕による異状摩耗)
	5	4	18	12 (")
	6	4	18	8 (")
	7	4	17	9 (")
	8	4	16	12 (")

[0015] A lifetime until it performs a cutting test in the cutting conditions in which the tool shown in ** and the following receives impact repeatedly and the maximum wear becomes 0.2mm is found, and the result is shown in Table 2.

Cutting conditions **ed material (round bar with 4 slots) S50C Hs32 cutting speed It sends 200m / min. It cuts deeply 0.15mm / rev. 2mm cutting oil It makes and is [0016]. It turns out that sublation was produced in early stages of use in the shock-proof examination to which a mechanical shock is applied, and trouble wear was caused by the result of Table 2 although the being clear difference had not come out in the scratch load. In addition, although the coat of a nitride was used in the example, the manufacture of the charcoal nitride of various composition proportion is also possible by adjusting the partial pressure of nitrogen, methane, etc. for the ambient atmosphere at the time of vacuum evaporation.

[0017]

[Effect of the Invention] the covering hard metal of this invention is compared with the conventional TiN and TiAlN, by making the element with low hardness add / dissolve, it excels in abrasion resistance and mechanical-shock-proof nature, and is markedly alike, and a long tool life is acquired moreover, the thing showing the effect which was excellent when it was applied to TiCN base cermet, although this invention had mainly explained the cemented carbide -- obvious -- it is .

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(54)【発明の名称】 被覆硬質合金

(57)【要約】

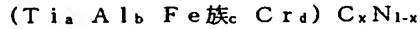
【目的】 本発明はPVD膜の残留圧縮応力が高い欠点を改善し、残留圧縮応力を低減することにより皮膜の密着性を高め、強いては被覆工具の耐剥離性を改善する技術を提供するものである。

【構成】 皮膜の主成分として、TiとAl及び/またはその固溶体の窒化物、炭窒化物より構成された0.5～10μmの膜厚から成る硬質皮膜をモル比において、

(Ti a Al b Fe族 c Cr d) C_xN_{1-x} と表した場合、a、b、c、d、xがそれぞれ0.3 ≤ a ≤ 0.7、0.3 ≤ b ≤ 0.7、0.01 ≤ c ≤ 0.2、0 ≤ d ≤ 0.1、0 ≤ x ≤ 1としたものである。

【特許請求の範囲】

【請求項1】 主成分としてTiとAl及び／またはその固溶体の窒化物、炭窒化物より構成された0.5～10μmの膜厚から成る硬質皮膜のTiの1部をFe族金属及び／またはCrで置換した被覆硬質合金の該皮膜組成をモル比において、



と表した場合、a、b、c、d、xがそれぞれ

$$a + b + c + d = 1$$

$$0.3 \leq a \leq 0.7$$

$$0.3 \leq b \leq 0.7$$

$$0.01 \leq c \leq 0.2$$

$$0 \leq d \leq 0.1$$

$$0 \leq x \leq 1$$

より成る範囲の皮膜であることを特徴とする被覆硬質合金。

【請求項2】 請求項1記載の被覆硬質合金において、Tiの一部をFe及び／またはCrで置換された(TiFeCr)の窒化物、炭窒化物の層とAlの窒化物から成る層を5層以上の多層にしたことを特徴とする被覆硬質合金。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本願発明は、耐摩耗性、耐欠損性に優れる切削工具として用いられる被覆切削工具部材及び耐摩耗工具として用いられる被覆耐摩部材に関する。

【0002】

【従来の技術】 従来PVD法による硬質皮膜は、TiNが主流であったが、最近TiCN膜があるいは(TiAl)Nといった新しい種類の皮膜が開発され注目されてきている。TiCNはピッカース硬さが3000近くあり、TiNのピッカース硬さ2200に比べ格段に硬く耐摩耗性を著しく高める効果も持つ。一方(TiAl)NはTiとAlの比率により異なるが、概略2300～2800のピッカース硬さを有し、TiNに比べ耐摩耗性を高める一方耐酸化性が著しく優れるため刃先が高温になる切削条件下などで優れた特性を発揮するものである。

【0003】 又、(TiAl)N膜の皮膜の改善としてTi/Alの比率を限定した特公平5-67705号や、(TiAlZr)N、(TiAlV)Nといった更に多元系の皮膜にした米国特許4871434号等が提案され、更に改善が計られている。しかしながらこれらの新しい皮膜は、上述の長所を有するものの皮膜に残留

する圧縮応力がTiN皮膜の1.5倍以上と高く、次のような種々の問題点を有するものである。

【0004】

【発明が解決しようとする課題】 皮膜の密着力は、皮膜の残留圧縮応力が高くなるほど弱くなるものであり、これら新しい皮膜はその密着性がTiNに比べ劣るものである。又、この残留応力が高いことは皮膜の密着性を悪くするだけでなく、膜厚が厚くなるに従い残留応力が増加するため皮膜の厚膜化への技術上の障害ともなり厚膜化が実現されていないのも現状である。

【0005】 残留圧縮応力を低減する最も簡単な方法は、被覆工程における被覆パラメーターを変更することが考えられる。本発明者は、アークイオン放電法により鋼基板上へTiNを3μm成膜する場合、被覆パラメーターである窒系分圧、バイアス電圧の残留圧縮応力を調べてみたところ、バイアス電圧-50Vにおいては-2GPa、同一-100Vにおいては-5GPaの残留圧縮応力を示した。又、窒系分圧を10⁻¹Pa下においては-1GPa、同10⁰Paにおいては-2GPaの残留圧縮応力を示した。この様に皮膜パラメーターを変えることにより容易に残留圧縮応力は変更可能ではあるが、アークイオン放電法やホロカリートほう等においては、それぞれの最適なパラメーターの範囲を有すること、及びパラメーターの変更により成膜される皮膜の膜特性が全く異なってしまうことにより、事実上、パラメーターを変更することにより残留圧縮応力を低減することは不可能であった。

【0006】

【本発明の目的】 本発明は上述の残留圧縮応力が高い欠点を改善し、残留圧縮応力を低減することにより皮膜の密着性を高め、強いては被覆工具の耐剥離性を改善すると同時に厚膜化をも可能とする技術を提供するものである。

【0007】

【課題を解決するための手段】 そこで本発明は、(TiAl)Nを基本にこれに各種元素を添加する検討を行った結果、次のような知見を得た。表1は3μm(TiAl)N皮膜をアークイオンプレーティング法により、バイアス電圧120V窒系圧力10⁻¹Paの条件下で成膜するときに種々の元素を添加した場合の残留圧縮応力を3μmのTiNの残留圧縮応力を1とした場合のそれぞれの残留圧縮応力を示す。

【0008】

【表1】

番号	膜質	残留圧縮応比力
従来例	1 TiN	1.0
	2 $Ti_{0.5}Al_{0.5}N$	3.1
	3 $Ti_{0.4}Al_{0.6}N$	3.2
	4 $Ti_{0.45}Al_{0.45}V_{0.1}N$	3.0
	5 $Ti_{0.45}Al_{0.45}Zr_{0.1}N$	3.0
	6 $Ti_{0.45}Al_{0.45}Hf_{0.1}N$	3.0
	7 $Ti_{0.45}Al_{0.45}Ta_{0.1}N$	3.2
	8 $Ti_{0.45}Al_{0.45}Nb_{0.1}N$	3.7
本発明例	9 $Ti_{0.45}Al_{0.45}Co_{0.1}N$	1.8
	10 $Ti_{0.45}Al_{0.45}Ni_{0.1}N$	1.4
	11 $Ti_{0.45}Al_{0.45}Fe_{0.1}N$	1.4
	12 $Ti_{0.45}Al_{0.45}Co_{0.05}W_{0.05}N$	2.5
	13 $Ti_{0.45}Al_{0.45}Ni_{0.05}Cr_{0.05}N$	2.0
	14 $Ti_{0.45}Al_{0.45}Ni_{0.05}Mo_{0.05}N$	2.3

【0009】表1より(TiAl)N皮膜中に軟質金属を分散、または固溶体化させることにより、膜中の残留応力が減少する傾向があることがわかる。よって、本願発明は、主成分としてTiとAl及び/またはその固溶体の窒化物、炭窒化物より構成された0.5~10 μ mの膜厚から成る硬質皮膜のTiの1部をFe族金属及び/またはCrで置換した被覆硬質合金の該皮膜組成をモル比において、 $(Ti_aAl_bFe_cCr_d)C_xN_{1-x}$ と表した場合、a、b、c、d、xがそれぞれ

$$a+b+c+d=1$$

$$0.3 \leq a \leq 0.7$$

$$0.3 \leq b \leq 0.7$$

$$0.01 \leq c \leq 0.2$$

$$0 \leq d \leq 0.1$$

$$0 \leq x \leq 1$$

より成る皮膜であり、さらにそれらの皮膜を5層以上の多層にして、厚膜化を達成したものである。

【0010】

【作用】(TiAl)化合物の皮膜中にFe族、Crを添加することにより、膜中の残留応力を減少させ、膜の耐衝撃性、特に断続切削等の機械的な衝撃に対しても剥離しにくい膜となる。さらに、Fe族の場合には合金化したターゲットを使用するとAlの一部を(CoAl)、(NiAl)等の化合物として形成でき皮膜の耐摩耗性、耐酸化性等をも合わせて改善できる。Cr族の場合も同様な効果があり耐酸化性・耐熱性等が改善される。以下、数値限定した理由に付いて説明する。

【0011】(TiAl)化合物膜中に固溶体/混合体として添加するFe族は、0.01未満では残留応力を低減するのに十分な効果がなく、0.2を越えると皮膜中のFe族の量が多くなりすぎ耐摩耗性、耐溶着性等が

劣化するため $0.01 \leq c \leq 0.2$ の範囲とした。また、(TiAl)化合物膜中に固溶体/混合体として添加するCrはFe族の含有量とも相関するが、Fe族と合金化させてその耐酸化性等を高めるものであり、0.1を越えて添加すると皮膜中のCrの量が多くなりすぎ残留応力の低減に十分な効果がなくなるため $0 \leq d \leq 0.1$ の範囲とした。尚、上記の元素はターゲット材として固溶体化しても、また各元素を個別のターゲットとして蒸着時に成分を調整してもさらに固溶体ターゲットと個別ターゲットを組み合わせても同様の効果をそうする。

【0012】皮膜中のCNの比率は、 $0 \leq x \leq 1$ 、すなわち炭化物、窒化物、炭窒化物の範囲としたのは、(TiAl)膜中に固溶体/混合体として添加したFe族、Crの効果により応力が緩和されるため、硬さの高い炭化物でも十分に使用でき、また硬さのやや低い窒化物、炭窒化物においてもFe族、Crの量を調整することにより十分な性能を有するため $0 \leq x \leq 1$ の範囲とした。

以下、実施例により本願発明を詳細に説明する。

【0013】

【実施例】84WC-3TiC-1TiN-3TaC-9Coの組成になるよう市販の2.5 μ mのWC粉末、1.5 μ mのTiC粉末、同TiN粉末、1.2 μ mのTaC粉末をボールミルにて96時間混合し、乾燥造粒の後、SNMA432のTAインサートをプレスし、焼結後、所定の形状に加工した。この超硬合金基体上にPVD法により、各種合金ターゲット、各元素単独のターゲットを用意し、表2に示すような皮膜を形成した。尚、比較のため従来例で記載した膜に付いても行った。次いで、これらの皮膜をスクラッチテスターにより、0から徐々に荷重を上げ、引っかいていき、膜が剥離する

荷重を求めた。それらの結果を表2に示す。

【表2】

【0014】

	磨費	磨厚	スクラッチ 強度 (N)	切削寿命 (min)
本発明合金	9	4	20	65 (正常摩耗)
	10	4	25	65 (")
	11	4	25	70 (")
	12	4	28	85 (")
	13	4	29	75 (")
	14	4	26	62 (")
従来例	1	4	20	25 (正常摩耗)
	2	4	25	35 (正常摩耗)
	3	4	22	32 (正常摩耗)
	4	4	18	8 (剥離による異状摩耗)
	5	4	16	12 (")
	6	4	18	8 (")
	7	4	17	9 (")
	8	4	18	12 (")

【0015】又、下記に示す工具が繰り返し衝撃を受ける切削条件にて切削テストを行い最大摩耗が0.2mmに達するまでの寿命時間を求め、その結果を表2に示す。

切削条件 被削材 (4つ溝付き丸棒) S50C
Hs32

切削速度 200m/min

送り 0.15mm/rev

切込み 2mm

切削油 なし

【0016】表2の結果により、スクラッチ荷重においては明確に違いがでていないが、機械的衝撃が加わる耐衝撃性の試験では使用初期に剥離を生じて、異状摩耗を

きたしたことが分かる。なお、実施例では窒化物の皮膜を使用したか、蒸着時の雰囲気や窒素、メタン等の分圧を調整することにより様々な組成比率の炭窒化物の製作も可能である。

【0017】

【発明の効果】本発明の被覆硬質合金は、従来のTiN、TiAlNに比べ、硬さの低い元素を添加/固溶させることにより、耐摩耗性・耐機械的衝撃性に優れ、格段に長い工具寿命が得られるものである。また、本発明は超硬合金を主に説明してきたがTiCN基サーメットに適用した場合にも優れた効果を現すことは自明である。